APPLICATION UNDER UNITED STATES PATENT LAWS

Atty. Dkt. No. PW 284117
(M#)

Invention: SHEET-SHAPED PRODUCT CONSISTING OF A THERMOSETTING RESIN MIXTURE AND CARBON FIBRES

Inventor (s): Hans Klaas VAN DIJK
Hans Hubertus Henricus HORNMAN
Bastiaan VAN VOORST
Peter DIJKINK

00909
Pillsbury Winthrop LLP

This is a:

- ☐ Provisional Application
- ☐ Regular Utility Application
- ☒ Continuing Application
  - ☒ The contents of the parent are incorporated by reference
- ☐ PCT National Phase Application
- ☐ Design Application
- ☐ Reissue Application
- ☐ Plant Application
- ☐ Substitute Specification
  Sub. Spec Filed ____________
  in App. No. ____ / ____
- ☐ Marked up Specification re
  Sub. Spec. filed ____________
  In App. No ____ / ____

SPECIFICATION

SHEET-SHAPED PRODUCT CONSISTING OF A THERMOSETTING RESIN MIXTURE AND CARBON FIBRES

The invention relates to a sheet-shaped product processable by means of flow moulding (hereinafter also referred to as "sheet moulding compound" or "SMC"), comprising carbon fibres and a thermosetting resin mixture based on a radical-curable resin as the matrix. The invention also relates to a process for the production of such a sheet-shaped product and to processes for producing net end products from such a sheet-shaped product.

As intended in this application, radical-curable resin is understood to be any resin containing an unsaturation and being capable of curing by radicals.

Sheet-shaped products processable by means of flow moulding which contain carbon fibres and a thermosetting resin mixture based on a radical-curable resin as the matrix are known. Such an SMC is for example described in CA-A-2199638. This reference however refers exclusively to the preparation of SMCs that are filled with fibrous material obtained via the chopped-strand technology. In practice, no such SMCs containing carbon fibres have however ever been marketed because such compounds cannot be produced via the normal compounding lines for glass-filled SMCs. The most important reason for this is that, after the

chopping, the carbon fibres do not show suitable distribution behaviour, as a result of which the compounds have an inhomogeneous fibre distribution and show non-optimum flow. In addition, an undesired amount of conductive dust is formed in chopping carbon fibres, with all the associated problems.

The aforementioned reference does describe sheet-shaped products consisting of a thermosetting resin mixture based on a radical-curable resin and fibrous material, including carbon fibres, but there are no indications that sheet-shaped products containing carbon fibres have actually been produced.

The aim of the present invention is to provide a sheet-shaped product comprising a thermosetting resin mixture based on a radical-curable resin and carbon fibres which does not possess the aforementioned drawbacks.

Surprisingly, a sheet-shaped product processable by means of flow moulding comprising carbon fibres and a thermosetting resin mixture based on a radical-curable resin as the matrix is obtained when the carbon fibres are present in the form of mats that consist substantially of carbon fibres with lengths of more than 1 cm, the volume percentage of the carbon fibres relative to the resin being less than 70% and the fibres moving freely relative to one another in the mat when the sheet-shaped product is in a mould subjected to a pressure so that, at that pressure and the lay-up percentage employed in the mould, a net end product with a homogeneous fibre distribution is obtained.

Using flow moulding for sheet-shaped products containing mats consisting of carbon fibres

with lengths of more than 1 cm in a matrix of radical-curable resin is not obvious. Although SMC technology in general has long been known, and mats consisting of carbon fibres have long been known per se, SMCs based on carbon mats have hitherto never been marketed.

In the case of SMCs based on aminoplasts, by contrast, using mats is assumed to be advantageous because the compounds have to be dried before the processing, which can for example be done by placing the impregnated mats on a chain conveyor.

Mats consisting of radical-curable resin containing (carbon) fibrous material are incidentally used in so-called hand-lay-up (HLU) or resin-transfer-moulding (RTM) techniques. Those techniques however involve the disadvantage that the required cycle times are relatively long and that only series of a limited size can be produced with them. An additional advantage of the present invention is that the SMCs according to the invention can be processed with cycle times like those that are customary in processing chopped-strand glass SMCs.

Wherever this application refers to "mats", they are understood to comprise both isotropic and anisotropic mats.

An 'isotropic mat' is understood to be a mat in which the orientations of the fibres show no regularity, but there is a random distribution of orientations. The carbon fibres in the isotropic mats generally have lengths of at least 1 cm.

An 'anisotropic mat' is understood to be a mat in which the orientations of the fibres show a certain amount of ordering. The fibres in an anisotropic mat may for example be grouped in bundles

that cross one another, for example perpendicularly. This also includes unidirectional (UD) mats. In the case of unidirectional carbon fibre reinforcement the use of a dispersed carbon fibre roving (or optionally of a number of dispersed carbon fibre rovings placed next to one another) is also regarded as "mats" as intended in the invention. A special case of a UD mat is a mat consisting of parallel fibre bundles, optionally of varying lengths, which moreover may or may not be staggered longitudinally with respect to one another.

In particular, continuous fibres are used in anisotropic mats. 'Continuous fibres' are understood to be fibres which substantially have a length that is larger than the mat's largest width. The maximum length of the fibres, in particular of the carbon fibres, is then determined by the maximum dimensions within the mat.

If the anisotropic mat consists substantially of continuous fibres, it may be advantageous to include a small amount of shorter fibres, for example fibres shorter than 6 cm, preferably shorter than 4 cm, in particular shorter than 2 cm, in the sheet-shaped product to obtain an even better distribution of fibres on bosses, ridges and rims. It has surprisingly however been found that even when the fibres substantially have lengths that are larger than the mat's greatest width, and in particular even when almost 100% of the fibres have lengths that are larger than the mat's greatest width, excellent 3-D end products with bosses, ribs, rims, etc. can still be obtained.

NEW PAGE 4a

It is to be noticed that in EP-A-0768340, in a paragraph presenting a general description of possible reinforcement materials which may be added to the very specific unsaturated polyester resin (SMC or BMC) compositions as are being taught in said reference, mentions carbon fibres as the last possibility in a long list of many other fibrous materials, and also presents a list of possible forms of such fibrous materials, including the form of chopped strand mats. There is no teaching whatever in EP-A-0768340 that indeed chopped strand mats are being used conveniently as the reinforcement material, and so there is even less suggestion that carbon fibre chopped strand mats would be used. In fact said reference rather would suggest the use of chopped strand fibres (see page 11, lines 56-59). Moreover, in all examples, comparative examples and figures of EP-A-0768340 where fibre reinforcement material is being used, such material consists glass fibre (rovings), which is being chopped.

It is to be noticed, moreover, that the object of EP-A-0768340 is to provide (reinforced) unsaturated polyester resin compositions, which can be moulded at a low temperature (40 to 100 °C) under a low pressure (0.1 to 10 kg/cm^2). Said aim is achieved by providing a specific mechanism of thickening (namely an alternative for metal oxide thickening): component (B) of EP-A-0768340 is a thickening agent containing powder of a thermoplastic resin as the effective component (in an amount of 20-120 parts by weight per 100 parts by weight of the unsaturated polyester). Thus, the compositions of EP-A-0768340 are necessarily different from the compositions according to the present invention, which contain metal oxide thickeners or thickeners equivalent therewith (usually in amounts of 10 parts by weight or less per 100 parts by weight of the unsaturated polyester). In other words, EP-A-0768340 teaches away from the present invention by replacing metal oxides (for instance, magnesium oxide) as thickener by another.

Besides the carbon fibres, the mats may also contain other fibrous materials. Examples are mats consisting of carbon fibres and (optionally metal-coated) glass fibres, carbon fibres and aramid fibres, or carbon fibres and steel fibres. These may be both isotropic and anisotropic combinations of fibrous materials. A combination of isotropic and anisotropic reinforcement is also possible, for example chopped random glass fibres with continuous UD carbon fibres. Combinations of isotropic and anisotropic reinforcement can also be realised with one type of fibrous material, for example UD carbon and random carbon in one mat.

The moulds may also be filled by stacking different types of compounds in the mould, for example by using a first SMC that contains for example UD reinforcement and a second SMC that contains for example random reinforcement.

The fibres in the mats can be bound together in different ways for the purpose of giving the mat sufficient mechanical consistency. This can for example be effected by connecting the fibres by sewing them together with a thread. This thread may be for example a polyester thread or a glass thread. It is also possible to use a polymer with a low melting point as the thread, such as PE or PP. Preferably use is made of a thread that softens at the processing temperature. To avoid any doubt it should be noted that the different ways in which the fibres in the mats can be bound together do not include binding together by means of weaving.

The fibres can also be stuck together by applying a binder. Preferably use is made of binders

that soften at the processing temperature or that dissolve in the resin mixture at that temperature. The employed amount of binder will usually be between 1 and 5 wt.% relative to the amount of fibre.

The volume percentage of the fibrous material (that is the total of the carbon fibres and any other fibrous material) relative to the resin must be less than 70%. This maximum is however reached only in the case of a unidirectional fibre reinforcement. In the case of biaxial or multiaxial reinforcement a maximum volume percentage of the fibrous material of 45% will usually be feasible. In the case of random fibre reinforcement the maximum volume percentage of the fibrous material will generally be about 30%. When one and the same mat contains a combination of the aforementioned types of reinforcements, the maximum volume percentages may differ from those mentioned above. A person skilled in the art will be able to easily determine what volume percentage of the fibrous material, depending on the type of fibrous material chosen and the type of carbon mats (i.e. the type of reinforcement) and on the resin chosen, will yield the best results.

Fibre contents that are very suitable for practical use are 40-60 volume percent in the case of UD reinforcement, 25-40 volume percent in the case of multiaxial reinforcement and 20-30 volume percent in the case of random reinforcement. A practical lower limit of the volume percentage of fibrous material will in all cases be approximately 10%. In all cases these percentages are relative to the total of fibrous material, resin and any fillers and other additives present.

The amount of resin mixture used per m^2 of fibrous material can incidentally easily be adjusted by removing resin mixture, for example with the aid of rolls. It is also possible to apply more or less of the resin mixture to the mats of the fibrous material by adjusting its viscosity. As described above, the surface weight of the fibrous material can also determine the amount of resin mixture absorbed.

In the invention a radical-curable resin, that is, a resin that contains an unsaturation capable of being cured by radicals, is used as the thermosetting resin mixture. Examples of such resins are: unsaturated polyester resins, vinyl ester resins and hybrid resins, such as polyester-polyurethane hybrids prepared via condensation of a polyester polyol with a di- or polyisocyanate followed by radical curing. A suitable example of such a hybrid resin are the DARON™ hybrid resins of DSM Resins. Suitable examples of usaturated polyester resins and vinyl ester resins are the SYNOLITE™ and ATLAC™ resins, respectively, of DSM Resins.

The viscosity of the thermosetting resin mixture may vary within a reasonable range, depending on the type of resin chosen, the type of mats, etc. A person skilled in the art will - in a relatively simple way - be able to find an optimum combination of the viscosity concerned, the type of mats, the volume percentage of the fibrous material, etc.

Providing sheet-shaped products comprising a radical-curable resin according to the invention and using a fibrous material in the form of carbon mats according to the invention results in a sheet-shaped

product that is extremely suitable for being processed by means of flow moulding.

Flow moulding is a technique in which sheet-shaped products are stacked and laid in a mould so that the mould surface is not entirely covered with the compound. The covered part is called the lay-up percentage. The mould is then closed and the compound is pressurised so that the mould is completely filled and a moulded part (net end product) with a homogeneous distribution of fibres throughout the entire moulded part is obtained. To this end it is necessary that, even when mats are used, the fibres in the mat can move freely relative to one another during the compression step.

Preferably the fibrous material in the sheet-shaped product consists entirely of carbon fibres. High mechanical properties are then obtained at a relatively low weight. Properties can then moreover be obtained which cannot be realised with other fibrous materials such as glass.

Preferably the carbon fibres are present in the sheet-shaped product in the form of an isotropic or anisotropic mat.

The surface weight of the fibrous material (carbon fibres and any other fibrous material present) may be chosen within a wide range. Suitable surface weights lie for example between 10 and 2,000 g/m^2.

Preferably a surface weight of between 150 and 700 g/m^2 is used. This results in an optimum combination of impregnation behaviour during the production of the sheet-shaped product and its flow properties during flow moulding.

The radical-curable resin in the sheet-shaped product according to the invention is most preferably an unsaturated polyester resin, a vinyl ester resin or a hybrid resin. The advantages of the product according to the invention will then be particularly evident. Particularly suitable unsaturated polyester resins, vinyl ester resins and hybrid resins have already been mentioned above. Such resins are commercially obtainable.

Preferably the radical-curable resin in the sheet-shaped product has an elevated viscosity as a result of thickening. This can for example be achieved through a reaction with a metal oxide or a diisocyanate (known as maturation of the compound). The viscosity required to produce moulded parts from the sheet-shaped products is determined primarily by the type of moulded part that is to be produced and by the type of mat used. This can easily be determined by a person skilled in the art.

The sheet-shaped product according to the invention may also contain all kinds of fillers. These fillers are the same as the usual fillers for sheet-shaped products based on for example unsaturated polyester resin. Chalk, calcium carbonate, clay, carbon particles, silica and/or metal particles are for example used as fillers. The sheet-shaped product may also contain catalysts, mould release agents, pigments and other common additives.

The invention also relates to a process for the production of a sheet-shaped product in which fibrous material (i.e. mats of carbon fibres and any other fibrous material present) is as described above impregnated with a radical-curable resin, after which

thickening of the resin to a desired viscosity takes place.

The sheet-shaped products thus obtained and thickened to the right extent can be very easily processed into products by means of flow moulding. The pressure employed in the flow moulding is generally between 20 and 200 10^5 N/m^2, preferably between 40 and 110 10^5 N/m^2. The usual moulding temperature, which also effects the curing of the radical-curable resin, is between 80 and 250°C, preferably between 110 and 190°C.

The products obtained in flow moulding (e.g. moulded parts) show very good mechanical properties as a result of the excellent flow of the product according to the invention during the flow moulding. Typical mechanical properties at a total carbon fibre content of 20-60 vol.%, e.g. with an unsaturated polyester resin as the matrix, are given in the following table for

(1) UD reinforcement (without filler)
(2) biaxial reinforcement (with and without filler)
(3) random reinforcement (with and without filler).

Measured values are specified for

- tensile strength; measured according to ISO 178, in MPa,
- tensile modulus; also according to ISO 178, in GPa.

Calcium carbonate was used as the filler.

Table:

	fibre/filler content [Vol.%]	tensile strength [MPa]	tensile modulus [GPa]
UD without filler	40-60 / 0	1100-1550	90-130
Biax. with filler	20-45 / 40	300- 700	25- 60
Biax. without filler	20-45 / 0	240- 650	20- 55
Random with filler	20-30 / 40	280- 400	25- 35
Random without filler	20-30 / 0	240- 350	20- 30

The sheet-shaped products are hence very suitable for use in the production of large moulded parts with for example ribs and bosses such as seat shells, housings, fittings, body parts for lorries and cars. The particularly good mechanical properties at - especially when carbon fibres are used - a low weight of the moulded parts obtained, their thermal stability, the moulded part's high heat deflection temperature and the excellent fatigue properties are then major advantages.

The invention also relates to a process for the production of moulded parts with a tensile modulus of > 20 GPa, in particular > 40 Gpa, and preferably > 70 GPa, a tensile strength of > 200 MPa, in particular > 500 Mpa, and preferably > 900 MPa, by flow moulding sheet-shaped products as described above.

The invention will now be elucidated with reference to the following example without being limited thereto.

Example 1.

A biaxial carbon fibre mat (40 cm wide, consisting entirely of continuous fibres) with a surface weight of 450 g/m^2 was on a small-scale SMC line impregnated with a hybrid resin, Daron™ XP-45 from DSM Resins, the Netherlands. The resin was then for 3 days thickened with a diisocyanate. A sheet-shaped product with a fibre content of about 31 vol.% was obtained. This sheet-shaped product was processed further with the aid of flow moulding in a mould (70% lay-up percentage) to obtain a three-dimensional object with bosses and ribs. Moulding was effected with the aid of a 360-tonne press (Diefenbacher) at a pressure of 100 bar. The sheet-shaped product showed excellent flow behaviour and the mould filled up entirely. A net end product with the desired bosses and ribs was obtained. The fibre distribution in the net end product obtained was homogeneous. Bar-shaped specimen were cut from flat parts of the end product obtained in order to determine the mechanical properties. The tensile modulus and tensile strength of these specimen, measured according to ISO 178, were 42.7 GPa and 535 MPa, respectively.